23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

LIFE CYCLE ASSESSMENT OF HYDROGEN PRODUCTION BY NATURAL GAS REFORMING IN BRAZIL

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Abstract. *The focus of this paper is on the life cycle assessment (LCA) of hydrogen production, via natural gas reforming, in order to examine its potential environmental consequences. LCA is a systematic set of procedures for calculating the environmental impact of a product or service through all stages of its life cycle. The analysis has been carried out considering engineering data obtained from a hydrogen plant demonstration project in Brazil. The size of this plant was set at 1,15E04 kg/year. An inventory was provided for the manufacturing, transport, and installation phases, as well as hydrogen production and equipment maintenance. The cumulative energy demand to produce 120 MJ was estimated at 1.82 E02MJ and the greenhouse gas emissions were at 1.59 kg* CO_2*eq. The following categories of impact were analyzed: acidification, global warming potential, eutrophication and ozone depletion. Results allow identifying the major impacts of the system components across the different impacts categories and issues of uncertainty data.*

Keywords: *life cycle assessment, environmental impact, hydrogen production, natural gas reforming, cumulative energy demand, global warming potential.*

1. INTRODUCTION

Hydrogen as an energy vector has been increasingly studied and already there is a reasonable consensus on its advantages in future energy systems. Different types of fuel cell technology (FC) can enable the energy use of hydrogen both in mobile and stationary applications, including small households, medium and large scale power plants (Sorensen 2004, 2005; Ballat, 2008; Babir, 2008 and Bartels, 2010).In internal combustion engines, hydrogen can be used pure or as a gas mixture mainly associated with natural gas. Successful experiences of hydrogen use in FC and internal combustion engines have been related to commercial vehicles (Martinez et al., 2010).

In this sense, political leaders, the scientific community and the major automobile companies have embraced hydrogen as the best option to respond quickly to threats posed by global warming and dependence on imported fossil fuels.

The enthusiasm for hydrogen is largely predictable, not only by the potential advantages as a fuel, but also by the diversity supply sources, which plays a significant role in the promise of energy independence. That is, hydrogen can be and is being produced from primary energy sources available freely in nature, both those that are renewable, such as natural sources that continuously renew themselves (water and biomass), as non- renewable, such as fossil fuels (coal, natural gas and oil), all largely composed of carbon and hydrogen atoms in different combinations (Fukurozaki, 2011).

Currently, hydrogen production on a large scale is used commercially in the manufacture of ammonia and methanol, as well as in the petroleum refining industry. Steam reforming and purification technologies are used to convert light hydrocarbons, natural gas, liquefied gas, oil, butane, and light naphtha into hydrogen.

For several decades, hydrocarbon steam reforming has been the more efficient, economical and widely used process in the hydrogen production. The dominant technology is the steam reforming of methane from natural gas, whose catalytic conversion produces hydrogen and carbon oxides.

Given the growing concern about the scarcity of natural resources and environmental burdens, the assessment of technologies, standardization and communication are interconnected tasks that require committed collaboration, planning and a broad view of researchers, entrepreneurs, consultants and public managers. This multi-purpose task aims to achieve higher performance technologies, to evaluate costs and benefits, to set standards and to produce reliable information procedure (Zucaro et. al, 2013).

The Life Cycle Assessment (LCA) is a method that proved to meet these interconnected tasks (Martinez et. al, 2013). Several LCA studies of the production and use of hydrogen have been published in the last decade, responding to a large number of problems and paving the way for future development of a low-carbon economy.

The focus of this paper is on the life cycle assessment (LCA) of hydrogen production, via natural gas reforming, in order to examine its potential environmental consequences. This study was performed according to the procedures and provisions suggested in the FC-HY Guide Manual (European Commission, FCH, JU, 2011) and ISO 14044 (2006).

2. MATERIALS AND METHODS

2.1 The investigated system

The system investigated was manufactured by Hytron Ltda (Campinas, São Paulo/Brazil) and designed for integrated with a FC technology (High Temperature Proton Exchange Membrane- HT-PEM). The main components of the Steam Methane Reforming (SMR) system are: desulfurization reactor, steam reforming reactor, high and low temperature shift reactors and heat exchangers and several special steel components (manifold, vessel and structural parts).

The reforming reactor and burners are located inside a pressure vessel, while all the other auxiliary systems, including power conditioning and the control system, are installed on a separate module. The entire system is installed on the same skid. The area of the SMR system is 5 m^2 approximately, for a total mass about 1,500kg. The standard operative temperature is around 600°C. The size of this plant was set at 1.15E04 kg of hydrogen per year and the expected service life time of a SMR system is 87,600 hours or 10 years.

The basic steps leading from natural gas to the hydrogen produce are: pretreatment of the raw feed, reforming to synthesis gas and conversion to hydrogen-rich gas product specifications (**Figure 1**). This basic SMR is supported by a process furnace, which provides heat to increase steam the gas temperature for the endothermic pretreatment and reforming process. The steam is used a reagent in both reforming and gas conversion. The furnace consumes natural gas as fuel and also process gas from SMR system (waste gas) and from FC technology (residual hydrogen).

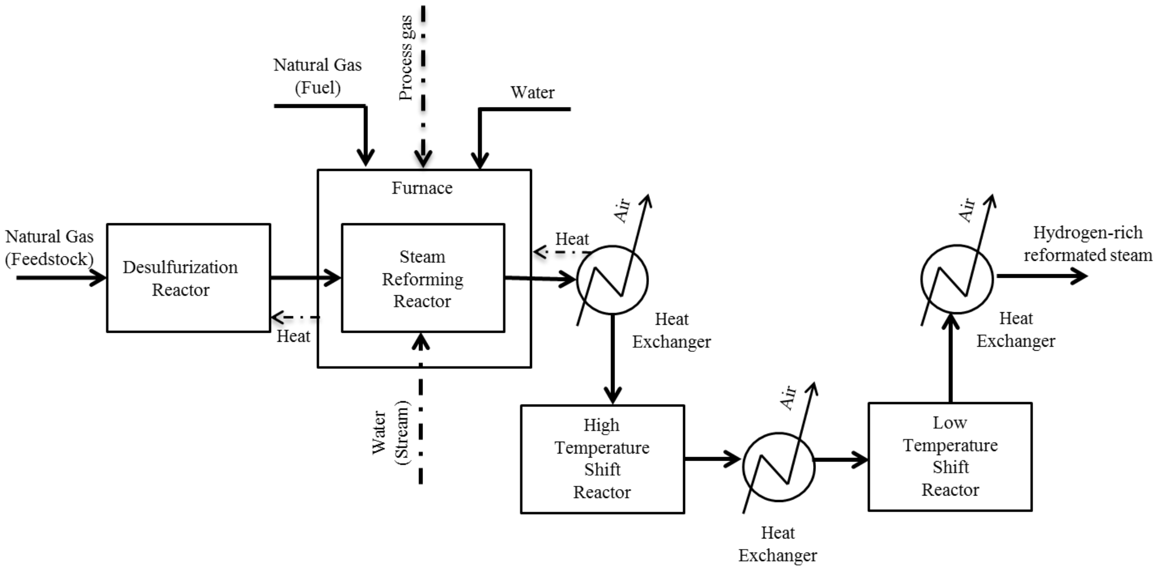

Figure 1- Schematic of Steam Methane Reforming process

Heat exchangers flue gas stream heat the feed for desulfurization reactor and reforming. The heat exchanger also extracts heat from furnace exhaust and from shift reactors for feedwater heating and evaporation process (heat recovery). Water (steam) used as reagent is partially recovery by condensation from the convert gas stream. Full representation off all these heat and materials interactions results in a model with multiple material and energy loops. Such multiple loops can be represented in ASPEN, but result in a model which is difficult to converge as parameters are varied to study implications of process design choices.

The SMR system studied here is designed to maintain material and energy loops that allow high conversion of fuel and reduce both the carbon monoxide content in reformatted gas supplied to the FC and in process gas consumed by furnace. The SMR system is claimed to meet the objective of clean production, meanwhile their features contribute to improve energy efficiency and to limit polluting emissions to the atmosphere.

2.2 Life cycle assessment

LCA is acknowledged as an important and comprehensive methodology to investigate the environmental impacts of products and services in which the concept of product life cycle can be understood intuitively. The product is evaluated from its “cradle”, where the materials and energy are extracted from natural resources through production and use to its disposal or “grave” (Baumann& Tillman, 2004). That is, the assessment starts with the extraction of resources to create the product, and ends at the point where all processed materials are returned to the environment.

The LCA process is systematic, iterative (**Figure 2**) and consists of four steps summarized by: I) definition of the objective and scope, II) analysis of inventory (LCI), III) impact assessment (LCIA) and IV) interpretation of results (ISO 14044, 2006). The focus of this tool is on two analytical modelling steps: the life cycle inventory and life cycle impacts assessment.

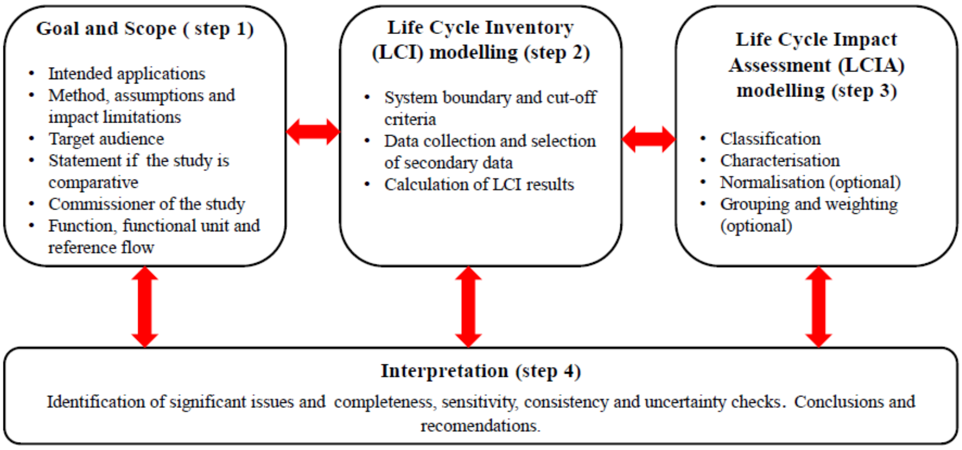

Figure 2- Life Cycle Assessment methodological steps

The Life Cycle Inventory (LCI) can be described as a technical system model used to produce, transport, use and dispose of a product. In the LCI, all relevant inputs and outputs of the system are compiled. The purpose of the LCI is to identify and quantify the resources required from the environment and the emissions generated to different environmental compartments.

The Life Cycle Impact Assessment (LCIA) is addressed to assess the environmental burdens related to extraction of resources and emissions to environment obtained in the inventory. Therefore, models of environmental mechanisms are used in which inventory results can be translated into potential impacts, such as climate change, acidification, toxicological effects to human health and ecosystems (Fukurozaki, 2011).

The results achieved of either the LCI or LCIA are interpreted accordingly with goal and scope in order to draw conclusions and useful recommendations for decision-making of different stakeholders. It can inform the choice of processes and products that are environmental friendly, and identify opportunities for improving environmental aspects, strategic planning, design or redesign; selection of environmental performance indicators and eco-labeling.

Since the entire system is studied, the environmental impact cannot be modeled at a very detailed level. Generally, economic and social aspects are not included in LCA unless they are used as a basis for characterization. Conducting LCA studies demands many efforts in exploring industrial systems; collecting and analyzing a large variety of data. However, one reason for conducting an LCA study is the growing concern about the environmental issues, expressed both by public opinion and government, as well the industry

These concerns range from the environment capability to meet the industry demand of materials and energy, ecosystems conservation to the issues of human health. Regardless of these concerns, in turn, it ultimately results in actions, regulations, changes in consumption and adaptations of industrial activities.

In general, the ACV has several features that make it attractive for use in engineering and industries (UNEP, 2005). This methodology has emerged as a qualitative, quantitative and structured analysis tool, which focuses in the technical systems to diversify concomitant environmental issues. That is, the trade-off between the environment and different stages of the product life cycle are better evidenced and understood when using LCA.

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2.3 Goal and Scope

The goal of this LCA is the identification and evaluation the most significant potentials impacts of the SMR system life cycle stages. The intended application of results focus both internal use in establishing guidelines for decision makers, as external use in the disclosure and dissemination of scientific knowledge of the hydrogen production by natural gas reforming under Brazilian conditions as an example case study. This is a non-comparative LCA study hence no different hydrogen production systems are compared.

A standard evaluation of environmental impacts (according to ISO 14044, 2006) and cumulative energy demand of the product system was undertaken. The endpoints impact categories are not investigated in this study. The impact method used is based on a CML 2.03 baseline 2000 (midpoint impact categories) developed by the Centre of Environmental Science at Leiden University. This study was carried out by means of the commercial SimaPro Analyst 8.02 software. This software allows manifold analysis, e.g. hotspot analysis (significant issues), uncertainty analysis (Monte Carlo analysis), and sensitive analysis.

Since this SMR system is integrated into the FC technology, the working hours assumed in this study is 40,000 hours. Over this time, the total amount of hydrogen produced is 6.27 E06 MJ (5.02E4 kg). This value represents the amount of energy (hydrogen) required for suitable electricity production by 20kW_{el} FC (High Temperature Proton Exchange Membrane). The **tables 1 and 2** show the reforming conditions used in this study and the mass and energy flows of natural gas consumption and production of hydrogen throughout the operation lifetime.

Table 1- Reforming conditions

Parameter	Baseline
Temperature	600ºC
Pressure	1.1 bar
Reformer efficiency	84.6%
Mass ratio of fuel to hydrogen	1.989 mol H_2/mol CH_4
Water into reformer	1.63 E-03 kg/s
Hour of operations	40,000 h

Table 2- Mass and energy flows of natural gas and hydrogen under operation lifetime

Flows	Mass	Density	Energy	Net calorific value
Fuel for reforming (NG) [1]	2.61 kg/h	0.8378 kg/Nm^3	4.18E06 MJ	40 MJ/kg
Fuel for heating (NG)	1.82 kg/h		2.91E06 MJ	
Hydrogen from reforming [2]	1.31kg/h	0.0899 kg/Nm^3	6.31E06 MJ	120 /kg

In this study we perform a cross-scale of environmental burdens associated with the manufacture of main SMR components, including relevant materials production and transport, maintenance and the production of hydrogen over working hours. Fuels and electricity, as well the key emissions to the air, water and soil have been taking into account for all processes. The system boundaries for SMR system are presented in the **figure 3**.

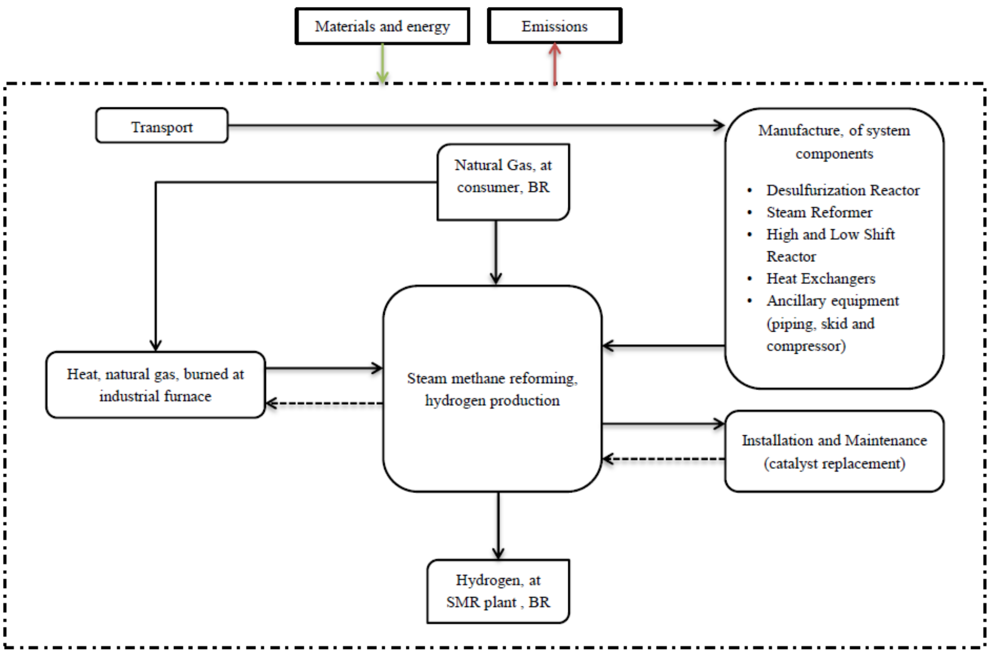

Figure 3- SMR system boundaries

The functional unit is to produce 120 MJ (net calorific value) of H_2 for FC stationary applications. The reference flow is 120 MJ/kg of hydrogen with 73.1 % purity and 0.4 bar @140ºC. The hydrogen production system is based on primary data from one SMR site (plant demonstration project located at Campinas, São Paulo), completed by commercial database. The geographic coverage of SMR system represents Brazilian boundary conditions and the reference years of SMR data are 2013-2015.

2.4 Life Cycle Inventory

The data sets consider the entire supply chain from natural gas production and natural gas supply; the manufacturing and maintenance of the main equipment and the hydrogen production (cradle to gate approach) suitable for directly use in FC technology at São Paulo state.

Data from existing high quality databases (e.g. Ecoinvent 2.02 and other non-SimaPro databases, i.e. Gabi databases) are used to supply the entire chain of materials and its transport, fuels and electricity. For instance, the data set for the electricity supply includes the whole electricity system life cycle (cradle to grave approach), as well as all relevant impacts and emissions for the provision of this energy in the country of interest.

The data from Ecoinvent 2.02 based on European characteristics related to natural gas production and distribution network processes were recalculated for Brazilian fuel production and distribution network conditions. Wherever possible, data especially derived with global geographic location have been employed.

Most of materials and process data of steam methane reforming system was provided by the manufacturing company. The main processes of SMRS studied here include the steam reforming itself, the CO-shift conversion and compression of hydrogen produced. However, the power conditioning and control system of SMR system are not investigated in this LCA, because these data are considered by the manufacturer as sensitive information.

2.5 Life Cycle Impact Assessment

The following mid-point impact categories have been considered for the evaluation of hydrogen production by natural gas reforming: Global Warming Potential (GWP), Acidification Potential (AP), Eutrophication Potential (EP), Ozone Depletion Potential (ODP) and Cumulative Energy Demand 1.08, divided in renewable primary energy demand (PED_R) and now-renewable primary energy (PED_{NR}). Within the software SimaPro Analyst 8.02, the CML 2.05 Baseline 2000 was selected as the most suitable method to calculate the mid-point contribution to the chosen impact categories. Since that normalization, grouping and weighting is not recommended by the FC-Hy Guide Manual, these optional steps of impact assessment are not carried out here.

3. RESULTS AND DISCUSSION

Results in **table 3 and 4** show the absolute values of the impact associated to manufacturing and installation, maintenance and operation of SMR system. Similarly, figures 4 and 5, presented the relative contribution of each phase studied.

Table 3 – Absolute values of potential environmental impacts related to the manufacturing and installation phase of a SMR system (120MJ)

Impact Categories	**AP** (kg SO_2 eq)	**EP** (kg PO_4--- eq)	**GWP100** (kg CO_2 eq)	**ODP** (kg CFC_{-11} eq)
Manufacturing (1) and installation of SMR sytem	Absolute values	Absolute values	Absolute values	Absolute values
Steam reforming reactor	2.56E-03	6.15E-04	3.16E-01	3.89E-08
Shift reactor equipment	3.97E-03	7.36E-04	3.65E-01	7.29E-08
Reformer ancillary equipment	3.57E-03	2.12E-03	5.64E-01	2.82E-08
Reformer Heat Exchange- HE	1.87E-03	6.99E-04	3.56E-01	1.70E-08
Radiator Heat Exchange HE	6.86E-04	3.30E-04	1.18E-01	5.95E-09
Desulfurization reactor	2.68E-03	1.38E-03	6.32E-01	5.73E-08
Series radiator HE equipment	1.72E-03	7.50E-04	3.43E-01	2.17E-08
Electricity production mix **(2)**	1.95E-07	5.56E-08	2.07E-04	7.81E-12

(1)- The manufacturing phase refers to the production of main components of SMR system.
(2)- The use of electricity presented in this table is only associated to the installation phase.

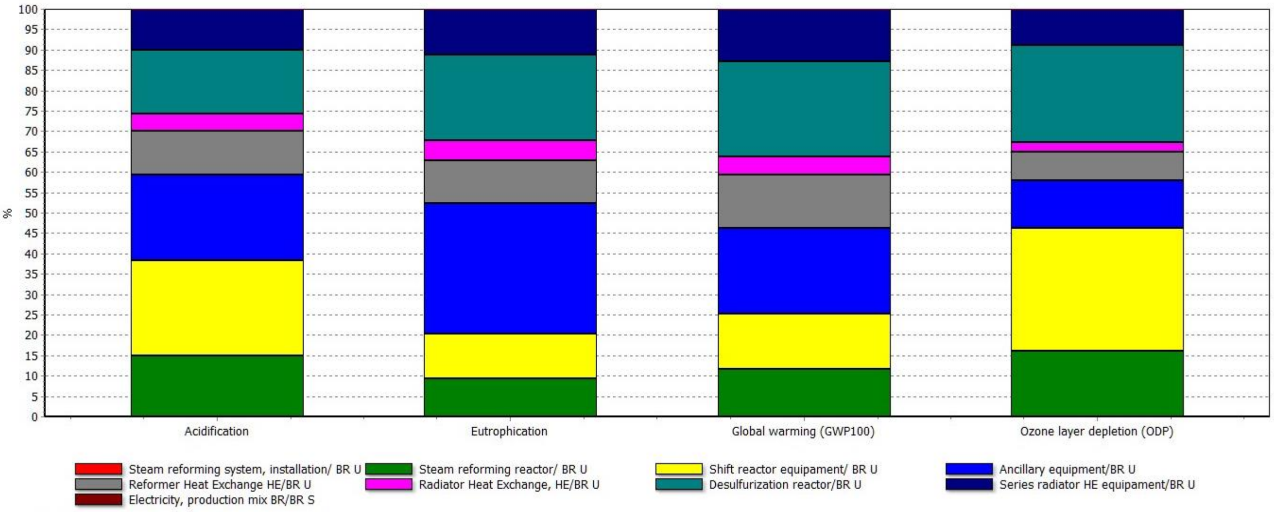

Figure 4- Relative contribution of the SMR system (120MJ) manufacture phase (equipment parts) and installation phase to selected environmental impact (%)

In the manufacturing phase of SMR system, the shift reactor equipment contributes most to the Acidification Potential with 23% contribution to the total. At the level of the shift reactor manufacturing, platinum extraction and processing into the catalyst used in this equipment part showed to be the largest contributor to the AP, with a contribution over 50% of the total shift reactor impact.

The ancillary components of SMRS (piping, pump and skid) have the highest impact on the Eutrophication Potential with a 32% contribution to the total phase. This contribution to the EP impact is related to the chromium steel18/8 and copper used for producing the ancillary components. The Global Warming Potential is most influenced by the desulfurization reactor at 24%, due to the zeolite used for the removal of SO_2 from natural gas streams.

The shift reactor is also the major contributor to the Ozone Layer Depletion Potential at 30%, given the extraction and processing of rare earths and subsequent production of cerium oxide used in catalytic converters. Comparatively, the use of renewable electricity of the country in the manufacturing and installation phase has a negligible impact on the all impact categories.

Table 4 – Absolute values of potential environmental impacts related to the hydrogen production and maintenance of a SMR system (120 MJ)

Impact Categories	**AP** kg SO_2 eq	**EP** kg PO_4^{---} eq	**GWP100** kg CO_2 eq	**ODP** kg CFC_{-11} eq
Hydrogen operation process	Absolute values	Absolute values	Absolute values	Absolute values
Natural gas, low pressure, for steam methane reforming	1.53E-03	6.61E-04	6.81E-01	9.82E-08
Water, deionised, at plant	1.66E-05	1.04E-05	3.54E-03	2.68E-09
SMR system, installation	4.71E-04	1.83E-04	7.43E-02	6.67E-09
Maintenance of SMR system **(1)**	8.85E-05	5.69E-06	8.41E-04	1.62E-10
Electricity, production mix BR	2.50E-04	7.14E-05	2.66E-01	1.00E-08
Heat, natural gas, burning in SMR furnace	1.33E-03	5.48E-04	5.60E-01	8.00E-08

(1) Maintenance of SMR SYSTEM is related with catalyst replacement, which is need every 40.000 hours.

The natural gas used for steam methane reforming itself and for providing heat dominates the environmental impacts during the 40,000 hours of operation phase. Practically all of the greenhouse gas impacts occur in this phase at 78%. Within the hydrogen production phase almost half of the impact of the GWP is caused by natural gas supply at 43%. The environmental burden associated with the natural gas supply is mainly due to the use of materials such as reinforced steel (29%) in the distribution network at high pressure and the natural gas consumption (10%) in their own offshore production process. The impact of the AP is dominated also by natural gas provide for the SMR system.

The process of steam methane reforming has the greatest AP impact (42%), followed by natural gas burned in an SMR furnace (36%). The Eutrophication Potential is also heavily influenced by these two operation processes (82%);

however the manufacturing and installation phase of SMR system has slightly greater impact share (12%). Ozone Depletion Potential is dominated by the steam methane reforming itself and heating process with an overall share about 90%. The natural gas supply contributes about 50% to the total, mainly because of energy usage in the transport of natural gas (long distance offshore pipeline). The maintenance process and the use of water have negligible impact on the all impact categories analyzed.

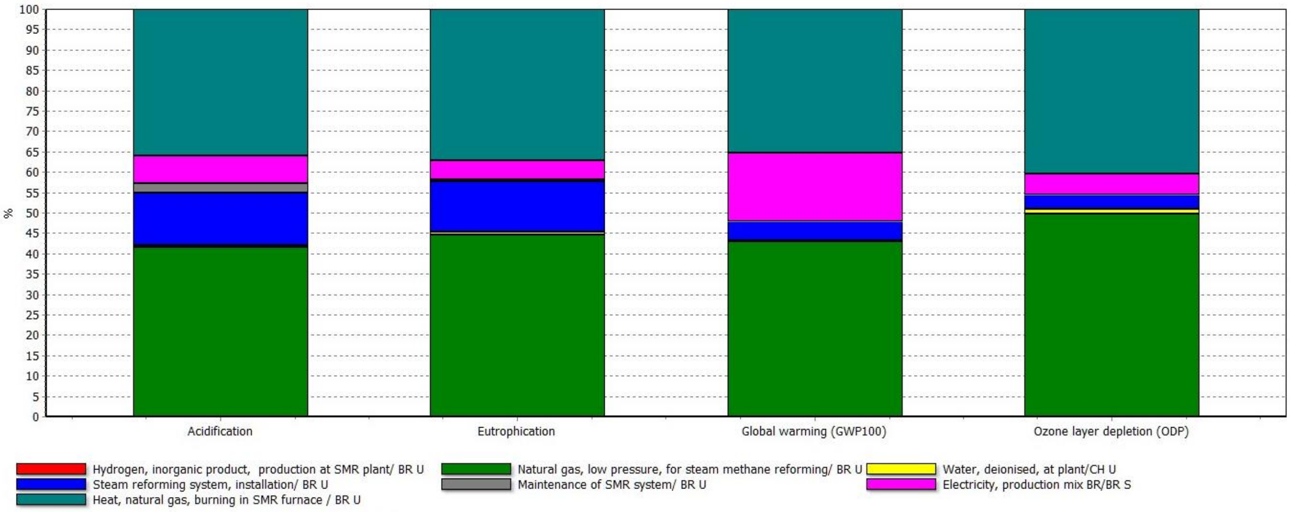

Figure 5- Relative contribution of the SMRS (120 MJ) production phase to selected environmental impact (%)

The required primary energy is provided by non-renewable energy (97%), which can be expected from natural gas steam reforming. 88% of the total PED (5.94 MJ) from renewable sources is found in the Brazilian Electricity Grid Mix (Figure 6). The total of primary energy demand to produce 120 MJ of hydrogen is 1.78E02 MJ from non-renewable energy and 4.85 MJ from renewable energy, sum up 1.82 E02MJ of CED.

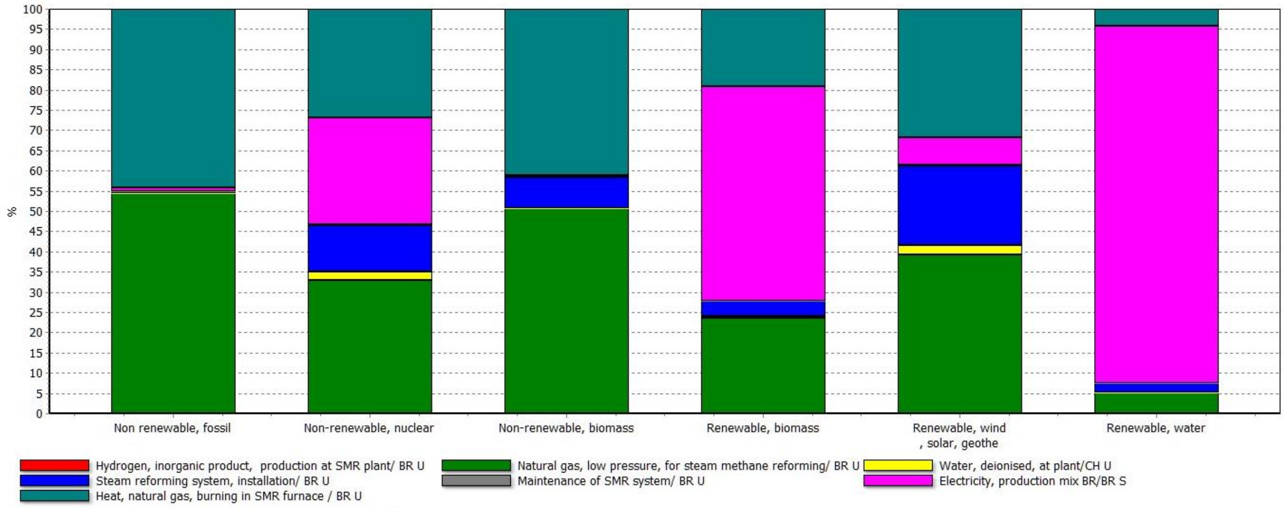

Figure 6. Relative contribution of SMR system life cycle (120 MJ) to Cumulative Energy Demand (%)

In the uncertainty analysis (95% of confidence interval), uncertainties for characterization LCIA impact categories shows that the major coefficient of variation (CV) is related to EP (31%), followed by the ODP (21%). The **table 5** shows the uncertainties for characterization LCA impact categories.

Table 5. Uncertainties for characterization LCA impact categories

Impact Category	Unit	Mean	Median	SD	CV	2.5%	97.5%	Std.Err. mean
AP	kg SO2 eq	0.00367	0.00356	0.000688	18.7%	0.00267	0.00533	0.00592
EP	kg PO4--- eq	0.00147	0.00137	0.000454	30.9%	0.000858	0.00252	0.00979
GWP100	kg CO2 eq	1.57	1.51	0.315	20.1%	1.1	2.33	0.00636
ODP	kg CFC-11 eq	1.97E-07	1.91E-07	4.1E-08	20.8%	1.34E-07	2.95E-07	0.00657

The parts of values that contain uncertainty data are about 61%. The most uncertain background data are those related to natural gas production included in the Ecoinvent 2.03 library available in SimaPro Analyst 8.02 software.

4. CONCLUSIONS

Only, the acidification potential, eutrophication potential, global warming potential, ozone layer depletion and cumulative energy demand are considered, and conclusions are drawn for these impact categories. In the manufacturing phase, the main components of SMR that contribute significantly in the impact categories studied are: the shift reactor, desulfurization reactor and auxiliary components, mainly because of its constituent materials, cerium oxide, zeolite and chromium steel, respectively. These materials together collaborate to a greater contribution to the acidification potential (cerium oxide), global warming potential (zeolite) and eutrophication potential (chromium steel). Both the installation and maintenance phase of the SMRS had negligible impacts compared with the other life cycle system phases.

On the other side, the hydrogen production phase was the greatest contributor to the total impacts of SMR system, in which the ODP, GWP and EP are those with most significant impact contributions. This is mainly due to the influence of the environmental load associated with the natural gas usage in the reform process itself and for the heating process.

The cumulative energy demand is predominantly non-renewable due the use of natural gas. Because the natural gas data production are from the reference year 2000, more current data can be used for more accurate results. Hence it is important; the data collected on natural gas consumed by the SMR system are high relevance for the overall results.

5. ACKNOWLEDGEMENTS

This work was supported by the National Agency of Petroleum, Natural Gas and Biofuels (ANP) and BG E&P Brazil Ltda. through the Investment in Research, Development and Innovation Clause, contained in contracts for Exploration, Development and Production of Oil and Natural Gas.

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